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A STUDY OF GAS SOLID REACTIONS AND AIR POLLUTION DETECTORS.(U)

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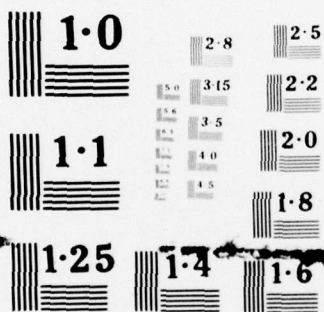
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
A basic research study was made for specific adsorbents which could be used for the detection of various air pollutants.		
The most promising adsorbents for various compounds were placed as coatings on a piezoelectric crystal detector, and the device was evaluated as a possible detector for the identification and analysis of these compounds. The nature of the basic reaction of the chemical compounds (solids) with these		

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pollutants was studied using infrared spectroscopy and oscillating crystals, and the interaction parameters were studied.

Quadrol and triethanolamine were good adsorbents for SO_2 ; Co-isonitrolo benzoyl acetone provided an excellent coating for organophosphorus compounds; ascorbic acid - AgNO_3 was used for assay of NH_3 , as were Ucon-75-H-90,000 and -Ucon-LB-300X, which were excellent for NH_3 and NO_x ; latex and nujol with trans- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ were good coatings for aromatic hydrocarbons; an acetone extract of a CCl_4 soot was excellent for the detection of H_2S ; and HCl was detected using trimethylamine · HCl .

FINAL REPORT

ARO GRANT NO. DAHC-74-G-0119

A STUDY OF GAS SOLID REACTIONS AND AIR POLLUTION DETECTORS

A. STATEMENT OF PROBLEM

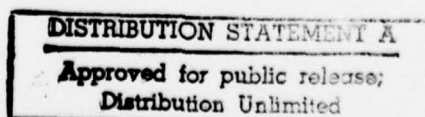
A basic research study will be made for specific adsorbents for the detection of various air pollutants. The substance is placed as a coating on a piezoelectric crystal and the device is evaluated as a possible detector for the identification and analysis of these compounds. The detector and each adsorbent will be evaluated with respect to sensitivity, linearity of response, speed of response, accuracy of response, limits of detection, stability, reversibility and selectivity of analysis.

B. RESULTS

Research during the last 3 years of the ARO grant was performed in 8 major areas: (1) SO_2 ; (2) organophosphorus compounds; (3) NH_3 and NO_x ; (4) aromatic hydrocarbons; (5) H_2S ; (6) HCl ; (7) CO ; and (8) detection of gases in solution. A total of 12 publications will result from this ARO-sponsored research, an average of 4 per year. A summary of this work by area is as follows:

(1) Assay of SO_2 . A new design for the coated piezoelectric crystal detector cell was made which is the most sensitive design for the cell ever made. Tri-ethanolamine and Quadrol were the new substrates used for the detection of SO_2 . The new design and the new coatings together make possible the selective detection of SO_2 even at ppb levels. (Publication 1).

Varying amounts of moisture in the air caused a problem in the determination of SO_2 in the air. The quadrol-coated piezoelectric crystal responds to moisture and therefore, the signals vary as the atmospheric moisture content varies. This problem is partially solved by using hydrophobic membrane filters. These filters reduce the moisture signal appreciably. The signal for SO_2 is also reduced somewhat by the filters. Even then, SO_2 could be measured as low as 10 ppb. This work is reported in Publication 2.



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The sensitive detector cell described earlier is too sensitive for SO_2 and the detector response levels off at the SO_2 concentrations larger than 50 ppm. For stack gas monitoring an insensitive cell design was used (one inlet and one outlet). Four layers of filter were used and atmospheric air is used as carrier gas. Samples of SO_2 in air were prepared and 5 ml of these samples were injected. The linearity of response is from 50 ppm to 700 ppm. SO_2 in air which is usually the range of stack gas concentrations of SO_2 . This detector uses quadrol coating and was tested in two oil refineries in Louisiana. Various stacks were shown to have SO_2 levels from 70-300 ppm. A good comparison with a commercial Bendix Gastec detector was obtained.

A portable instrument was built using a piezoelectric crystal detector with a quadrol coating. The power for the frequency meter, oscillator and a small air circulation pump was obtained from a 12-volt car battery. The portable instrument was tested in the University parking lot, samples being taken directly from car exhausts for injection into the detector. It was observed that an old VW produces about 1-1/2 times more pollution than an Opel fixed with an air pollution control device. The SO_2 concentrations in the exhaust are in the range of 30-50 ppm. About 3 feet away from the exhaust the reading showed only 8 ppm SO_2 . Observations with other cars is in progress. We hope to obtain a mixing device for obtaining known SO_2 -air mixture flows for calibration purposes. (Publication 3).

(2) Organophosphorus Compounds. A quartz piezoelectric crystal coated with the Co complex of IBA (isonitrilo benzoylacetone) has been used for the detection of organophosphorus pesticides via selective sorption. The crystal is incorporated in a mixer circuit to allow read-out of either an ammeter or a recorder, and is sufficiently sensitive to allow detection of organophosphorus compounds at levels of a part per billion. This detector has a potential for use both as an air pollution sensor and a highly selective gas chromatography detector. It is completely specific for organophosphorus compounds. Furthermore, the detector can be made completely specific for one organophosphorus compound by using that compound in a tertiary complex with Co and IBA. (Publication 4).

(3) Detectors for NH_3 , NO_x and Organo Nitrogen Compounds. The new cell design described by us (Publication 1) was used for the detection of NO_2 and NH_3 . Various coatings were tried for each gas. Out of the coatings tried, Ucon-75-H-90,000 and Ucon-LB-300X (obtained from Analabs Inc., Connecticut) proved to be satisfactory coatings for NO_2 and NH_3 . The above substrates were applied to the surface of piezoelectric crystals, and the crystals were then exposed to NO_2 gas. IR spectroscopic study of these reactions have revealed that the compounds of the type R-O-NO (covalent nitrite) and R-NO (nitroso) are formed by the reaction between the Ucons and NO_2 . With these coatings and with the new cell design it has been possible to detect NH_3 and NO_2 as low as 1 ppb. Interferences were minimal. (Publication 5).

Ammonia was detected using a coated piezoelectric quartz crystal. The adsorption of ammonia on a crystal coated with an ethanol extract of Capiscum Annuum Variety was linear with concentration from 10 to .001 parts per million (ppm) of NH_3 in air. Frequency changes ranged from 120 Hz for 10 ppm to 50 Hz for .001 ppm when 10 ml samples were injected. When silver nitrate was added to the crystal surface, the frequency changes were increased to 75 Hz for 10 ppm and 15 Hz for .001 ppm for 1 ml samples. The main active ingredient in the Capiscum Annuum extract is thought to be ascorbic acid. When pure ascorbic acid was used as a crystal coating, frequency changes ranged from 160 Hz for 10 ppm to 60 Hz for .001 ppm for 1 ml samples. Adding silver nitrate to the ascorbic acid surface gave frequency changes of 320 Hz for 10 ppm and 70 Hz for .001 ppm, 1 ml samples. Thus, the coating of ascorbic acid is shown to be a sensitive coating for the detection of ammonia over a wide range of concentrations. These coatings were also shown to be active toward organic amines, such as triethylamine and butylamine, with frequency changes within the same order of magnitude as those shown by ammonia. The mechanism of these reactions is thought to be primarily an acid-base reaction. (Publication 6).

Recently, it was shown that a crystal coating of chlorophyll extracted from spinach leaves adsorbs relatively large quantities of ammonia and produces a very sensitive ammonia detector. Frequency changes as high as 900 Hz for 1 ppm

NH_3 and 1400 Hz for 10 ppm were measured. However, the coating was also very sensitive to atmospheric humidity which caused measurements to be erratic and caused an erratic recorder baseline. This problem has been corrected. Porphyrin compounds similar to chlorophyll were investigated as possible gaseous pollutant detectors. Hemin and hemoglobin showed little activity toward ammonia; other metal porphyrins will be investigated in the near future. The preliminary experiments with chlorophyll suggest that the chlorophyll coated crystals may not show response to the large range shown by ascorbic acid but the slope of the calibration curve is much greater and should provide a more accurate ammonia assay.

Ammonia detectors based on these crystal coatings represent a significant technological advance since previous piezoelectric detectors required a dry nitrogen atmosphere and required activation by NO_2 ; and for a detector to obtain an optimum usefulness it must be used under ambient conditions. The large range of sensitivity shown by the ascorbic acid-silver nitrate coated crystal makes it especially useful for remote sensing and monitoring. The chlorophyll coated crystal should prove to be quite useful where accurate concentrations over a more limited range are necessary. (Publication 6).

(4) Detection of Aromatic Hydrocarbons. Nujol with trans- $\text{IrCl}(\text{CO})_2(\text{PPh}_3)_2$ complex was used as a coating on the piezoelectric crystal detector for the preferential detection of aromatic hydrocarbons in air in the presence of aliphatic hydrocarbons and other pollutants. The effect of atmospheric moisture is minimal, and interference from other gases and vapors is small. This detector was also used to monitor auto exhausts for aromatic hydrocarbons. A paper on this work has been accepted by Environmental Letters. (Publication 7).

The investigation of coatings which utilize a latex coating for the detection of aromatic hydrocarbons in a static environment has continued. Calibration curves of concentration vs. frequency are linear in the range 10 - 200 ppm for various aromatic hydrocarbons.

(5) Assay of H_2S . The search for an inorganic crystal coating for the detection of H_2S has continued and none has been found which is superior to the Ni(EDTA) complex previously reported. This coating is quite sensitive to H_2S , but results are at present not reproducible. This irreproducibility is believed to result, at least in part, from the adsorption of atmospheric moisture. Work will continue to control this variation.

Fluorescein mercuric acetate which is reported to react fast with H_2S in solution did not show much activity for H_2S when used as a coating on the crystal. H_2S was observed to give irreversible adsorption on most of the coatings tried and therefore, these coatings were of little use.

A new coating was developed for H_2S , a carbon residue obtained by burning of chloroform in air. The residue contains 3-4 compounds which can be seen as yellow, brown, gray and black spots on a thin layer silica gel separation. We have observed that out of these compounds the black residue (which is insoluble in common solvents) is the active substrate. Chloroform is burned on a spatula in air and the black residue formed on it is applied on the surface of the crystal; this carbon coating has shown a very good response for H_2S . The linearity of response is observed from 1 ppm to 100 ppm. Atmospheric moisture has no effect on this crystal coating.

Complete reversibility can be achieved by removing the crystal from the cell and blowing hot air on the surface. The chemical nature of the carbon black and the nature of the reaction with H_2S was studied. Carbon blacks obtained from burning of other organic compounds such as benzene, CCl_4 , acetone, etc., do not show sensitivity for H_2S . The carbon black obtained from chloroform burning appears to be a promising substrate for H_2S . Crystals coated with the acetone extracts showed a linear response to H_2S in the concentration range 1 to 100 ppm. However, the response becomes slow as concentration is increased limiting the upper limit of usefulness to about 60 ppm. The Department of Labor's Occupation Safety and Health Administration lists 20 ppm as the acceptable ceiling

concentration of H_2S , thus these crystal coatings measure within the range of interest. The acetone extracts of the chloroform soot produced a frequency change of about 30 Hz for a concentration of 10 ppm H_2S , while the acetone extract of chlorobenzoic acid, produced about 135 Hz for that concentration. Thus, the chlorobenzoic acid extract is the better coating. Experiments are presently underway to characterize the active ingredients and other soots are being prepared so that the response time and frequency changes can be optimized. The experiments reported above were carried out using a crystal with silver electrodes. Coated crystals using gold electrodes did not respond to H_2S ; crystals with nickel plated gold electrodes did respond but at a much lower level than silver electrodes. (Publication 8).

H_2S is a dangerous gas which has presented a safety problem to a number of American industries. This is especially true since H_2S at a dangerous level is not noticed by workers and levels can increase suddenly. This commonly occurs in closed working areas and mine shafts. Thus, the development of a piezoelectric H_2S detection device represents an important impact on industrial and mining safety. Existing H_2S detection systems are usually not portable while a piezoelectric detecting system can be developed which is portable and even small enough to carry in the workers' pocket.

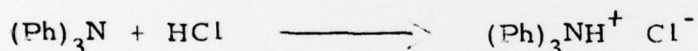
Several new inorganic and organic compounds used as coating materials were investigated and were found to be active toward hydrogen sulfide: 1,2-naphthoquinone-4-sulfonic acid, thiosemicarbazide, 1-nitroso-2-naphthol $CdCl_2$, $Pb(Ac)_2 \cdot 3H_2O$, $AgOAc$ (in n-butylamine) and methanolamine. Two promising coating materials have been found which are able to detect H_2S in the ppm range; silver acetate and triethanolamine. The frequency changes ranged from 300 Hz for 10 ppm to 55 Hz for 0.01 ppm, when silver acetate was used as the coating material. No interference was observed from NH_3 , NO_2 , SO_2 , CO moisture and organic vapors.

(6) Detector for HCl. Hydrogen chloride gas is a noxious byproduct of many industrial processes. In order to monitor the gas content in the atmosphere, a sensitive hydrogen chloride monitor is needed.

The detection of hydrogen chloride has been accomplished by the use of a piezoelectric crystal coated with different tertiary amines. A successful technique for placing these amines on the surface of a piezoelectric quartz crystal is to vapor deposit the amines on the crystal surface in a three-neck flask using vacuum and heating. The amount of amines deposited can be monitored during this process and reproducible coatings are possible.

The adsorption of hydrogen chloride on a crystal coated with triphenylamine was linear from 0.1 - 100 ppm concentration range in air.

The mechanism of this detection is believed to be the binding of the lone nitrogen electron pair of the amine compound to the extremely polar hydrogen chloride at each site according to the next reaction :



Other amines were investigated for detection of hydrogen chloride in the ppm range. Among these the most sensitive was the trimethylamine · HCl.

The detection of hydrogen chloride has been accomplished by the use of a crystal coated with different tertiary amines. The adsorption of hydrogen chloride on a crystal coated with trimethylamine · hydrogen chloride was linear in the 0.001 - 100 ppm range in air. At 100 ppm the frequency change was about 470 Hz and at 0.001 ppm, it was about 120 Hz, respectively. Atmospheric humidity, CO, SO₂, H₂S, TMA and NO₂ gave a very small response at 1000 ppm; no interferences were obtained. Ammonia at 100 ppm showed a strong irreversible reaction. Other organic compounds were investigated for detection of hydrogen chloride: galactosamine · HCl, hydroxylamine · HCl, cadaverine · HCl, L-ornithine · HCl, semicarbazide · HCl, etc. Among these, the most sensitive was the L-ornithine · HCl; at 100 ppm the frequency change was about 550 Hz and at 0.001 ppm it was about 210 Hz, respectively. Work will continue to investigate the reproducibility. (Publication 9).

(7) Detection of Carbon Monoxide. The search for a specific coating for the detection of carbon monoxide has continued. Many different inorganic and organic compounds were investigated with little or no success. Among these were n-butylamine-silver acetate; tetramethylene pentamine; sulfamylbenzoic acid; ethylenediamine-cupric sulfate; quadrol-ethylenediamine; LaCrO_3 ; anhydron $[\text{Mg}(\text{ClO}_4)_2]$; glycine-ethyl-ester $\cdot \text{HCl}$ activated by NO_2 .

Many new compounds were investigated at different experimental conditions; experiments were performed not only at room temperature, but also at higher temperatures ($40 - 60^\circ \text{C}$). Bis(chlorodicarbonyl) rhodium, hemoglobin (human and beef), hemin (beef), cytochrome C (equine heart) and histamine were investigated. Some of these materials may provide a viable carbon monoxide detector, but further experiments are necessary to find the most sensitive coating material.

A promising group of coatings has been found which will detect low levels of CO; this is a group of sugar alcohols and sugars. The best coating has been provided by the sugar alcohol, mannitol which gave frequency changes of 70 Hz for 10 ppm CO and 134 Hz for 100 ppm CO. However, this activity was achieved only after activation by nitrogen dioxides which the coating also quantitatively adsorbs. The linear concentration range for NO_2 adsorption and frequency changes was 120 Hz for 1 ppm to 210 Hz for 6 ppm. Further experimentation is necessary to determine if a method for detection for CO can be developed.

This quantitation detection of low levels of CO by NO_2 activated mannitol represents a considerable technological advance. A large number of potential CO active coatings have been investigated in the past, with little or no success. So, even though the mannitol coating may not provide a viable CO detector, it shows that the detection of CO by a coated piezoelectric crystal is possible and that this line of research may prove productive. Compact CO detectors, which can be provided by piezoelectric crystals, are of great need in industry and wherever incomplete combustion is possible, since the tasteless, odorless CO gas represents a major hazard.

(8) Detection of Gases in Aqueous Solution. Research has been expanded to include detection of gases in a water solution using coated piezoelectric crystal devices. Ammonia and H_2S gases in water have been detected. This detection was accomplished by the isolation of the crystal from the solution using a membrane which was permeable to gases but only sparingly permeable to water. By injecting ammonia into a solution with which the membrane had contact, concentrations from 3×10^{-4} to 3×10^{-3} moles per liter total ammonia were detected by frequency differences from 150-800 Hz with reasonable linearity. For H_2S , gas concentrations from 2.25×10^{-5} to 2.25×10^{-4} moles per liter of water were measured by frequency differences from 50 - 1500 Hz, also with reasonable linearity. Piezoelectric devices are potentially more sensitive than the more accepted analytical devices. These preliminary experiments show that piezoelectric devices can be used to detect gases in solution. (Publication 10).

(9) Review Articles. Two reviews on applications of the piezoelectric crystal detector in analytical chemistry have been published. (Publications 11 and 12).

C. LIST OF PUBLICATIONS

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